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(54) Polyamide 4.6 composition.

(57) The invention relates to a stabilized polyamide 4.6 composition, which per 100 parts by weight of polyamide contains 0.001-0.2 parts by weight of copper in the form of an insoluble copper salt and 0.1-25 parts by weight of a halogen-substituted organic compound. The composition is particularly suitable for electric/electronic applications.

EP 0 390 277 A1

POLYAMIDE 4.6 COMPOSITION

The invention relates to a copper-stabilized polyamide 4.6 composition. The use of copper compounds, in particular copper salts, such as copper halides, as stabilizer of polyamides is known. The JP-A-86-289660 points out the particular effect of the presence of potassium iodide besides the copper salt, copper iodide, giving very good thermal stability of polyamide 4.6 for a very long time. The use of copper iodide alone only gives a marginal improvement of the thermal stability. In the case of polyamide 4.6 used in for instance electric and electronic equipment, however, the presence of free potassium iodide is not allowed because of the high risk of corrosion and frequently too high conductivity of the material.

The most obvious solution for stabilizers of polyamide 4.6 compositions in electrical/electronic applications consequently lies in the use of non-ionogenic organic compounds with a stabilizing effect.

However, an extensive examination of the commercially available stabilizers and stabilizer combinations did not yield an organic non-ionogenic stabilizer meeting the high stability requirements at the elevated temperatures that are necessary for many electronic/electric applications. Very surprising, it is now found that a combination of an in water insoluble copper salt in a very low concentration with a halogen-substituted organic compound has an unexpectedly strong stabilizing effect in polyamide 4.6 compositions.

The polyamide 4.6 composition according to the invention is characterized in that per 100 parts by weight of polyamide 4.6

(a) 0.001-0.2 parts by weight of copper in the form of an in water insoluble copper salt, and

(b) 0.1-25 parts by weight of a halogen-substituted organic compound are present.

The insoluble copper salts preferably contain monovalent copper. Cu(I) iodide appearing to be very suitable. The halogen-substituted organic compound is in principle any compound covered by this definition. For practical reasons, processability and safety, preference is given to compounds which are stable and are little volatile at the processing temperature of polyamide 4.6, i.e. 300-330 °C. Such compounds are in general high-molecular and/or have a high halogen content; particularly suitable are halogen-substituted epoxy and styrene oligomers or polymers. These compounds are suitable in particular if they have a high bromine content. In that case there is the special advantage that the composition is also flameproof. It should be noted that it is very surprising that bromine-containing compounds have a synergetic effect in combination with a Cu(I) iodide.

Examples of such bromine-containing high-molecular styrene and epoxy compounds are commercially available under different names.

Example:

Pyrocheck 68 PB from the firm of Makhteshim and Makhteshim F2400 from the firm of Makhteshim.

Due to the very low Cu(I) iodide content of the composition, at least 0.001 parts by weight per 100 parts by weight of polyamide in order to obtain a significant effect, up to a maximum of 0.2 parts by weight - at higher concentrations no further improvement of the stabilization occurs - , the conductivity of the composition remains within the applicable standards. By preference the Cu(I) iodide concentration is between 0.003 and 0.1 part by weight per 100 parts by weight of polyamide 4.6.

The concentration of component (b) in the composition can vary between wide limits. In order to obtain some effect, at least 0.1 part by weight per 100 parts by weight of polyamide is present. When more than 25 parts by weight of component (b) is present, no further improvement of the stability is achieved and the mechanical properties of the composition are affected. In particular, if compounds with flame-retardant properties are used the concentration is in part chosen on the basis of the effect thereof. Preferably, the concentration of (b) in the composition is between 0.5 and 15 parts by weight of b per 100 parts by weight of polyamide 4.6.

By 'polyamide 4.6' is understood in this context a polyamide which is substantially composed of tetramethylene adipamide units. 'Substantially' means here at least 50%, preferably at least 80%. Besides the tetramethylene adipamide units the polyamide may contain other polyamide-building units, such as caproamide, dicarboxylic- and diamine-derived units, polyester-and/or polyimide-building units.

The polyamide 4.6 composition may further contain the usual additives and fillers, for instance release agents, pigments and colorants, reinforcing fibre materials, lubricants and other polymers. Other polymers are for instance polystyrene, polyacrylate, polyarylate, polyolefine, polyester, polyeth r and polysulphon,

other polyamides and thermosetting resins for instance ph nol resins and melamine.

The composition according to the invention can be prepared using the customary techniques of melt mixing and dry blending. Known apparatus used for this are for instance extruders and Banberry blenders. Preferably the mixing is done in an inert gas atmosphere. With the customary techniques the composition according to the invention can be processed from the melt into objects, for instance by means of injection moulding, extruding and compression moulding.

The invention will now be elucidated with the following examples and comparative experiments, without however being restricted thereto.

Examples and comparative experiments

In all examples and comparative experiments the composition was prepared on a ZSK 30 Werner and Pfleiderer twin-screw extruder, with the temperature set at 300 °C.

Injection-moulded test bars were made from the compositions; melt temperature 315 °C, mould temperature 80 °C. Test bars according to DIN 53455/4. These test bars were subjected to ageing tests by exposition to atmospheric conditions at elevated temperature in an air oven.

The tensile strength according to ISO-R 527/2 was determined as a function of the exposition time.

The time elapsed until the tensile strength of the bars had diminished to half the initial value is shown in Table 1 for each of the compositions examined.

CuI: Copper iodide, chem. pure

KJ: Potassium iodide, chem. pure

Irg. 1098: Irganox 1098, N,N′-hexamethylene bis(3,5-di-tert. butyl-4-hydroxy hydrocinnamic amide) from CIBA-GEIGY, Switzerland

PEPQ: Irgafos P-EPQ, a dimerphosphonide, from CIBA-GEIGY, Switzerland

Perm. DPPD: Permanax DPPD, N,N′-diphenyl-para-phenylene diamine, from Vulnax International Ltd., UK

P-68PB: Pyrocheck 68PB, a brominated polystyrene compound, from Makhteshim, Israel

PA 4.6: Polyamide 4.6, from DSM, Netherlands, ηrel = 3.4

TABLE 1

Examples I-IV and Comparative Experiments A-E	
Composition	Half-value time (150 °C)
wt.%	hours
A. 0.0075 CuI (wt.% Cu)	750
B. 0.0150 CuI (wt.% Cu)	1200
C. 0.030 CuI (wt.% Cu)	1200
D. 0,030 CuI + 0.24 KI (wt.% I)	3000 *)
E. —— 15 P-68PB	220
I. 0.0075 CuI + 15 P-68PB	2400
II. 0.0150 CuI + 15 P-68PB	2400
III. 0.030 CuI + 15 P-68PB	2500
IV. 0.030 CuI + 0.24 KI + 20 P-68PB	4000 *)

*) Conductivity too high for electric/electronic applications

TABLE 2

Comparative experiments F-K	
F. 1.0 Irg 1098	750
G. 1.0 Irg 1098 + 10 P-68PB	700
H. 1.0 Perm DPPD	750
I. 1.0 Perm DPPD + 20 P-68PB	900
J. 0.4 Irg 1098 + 0.4 PEPQ	750
K. 0.4 Irg 1098 + 0.4 PEPQ + 20-68PB	830

Claims

1. Copper-stabilized polyamide 4.6 composition, characterized in that per 100 parts by weight of polyamide 4.6
(a) 0.001-0.2 parts by weight of copper in the form of an in water insoluble copper salt, and
(b) 0.1-25 parts by weight of a halogen-substituted organic compound
are present.

2. Composition according to claim 1, characterized in that the copper salt is Cu(I) iodide.

3. Composition according to claim 1 or 2, characterized in that the halogen-substituted organic compound is a brominated epoxy or styrene oligomer or polymer.

4. Composition according to any of the claims 1-3, characterized in that 0.003-0.1 part by wt. of component (a) is present.

5. Composition according to any of the claims 1-4, characterized in that 0.5-15 parts by weight of component (b) are present.

6. Application of the composition according to any of the claims 1-5 in electric or electronic applications.

7. Copper-stabilized polyamide 4.6 composition as substantially described in the specification and the examples.

Claims for the following Contracting States: ES, GR

1. Process for the preparation of a copper-stabilized polyamide 4.6 composition, characterized in that per 100 parts by weight of polyamide 4.6
(a) 0.001-0.2 parts by weight of copper in the form of an in water insoluble copper salt, and
(b) 0.1-25 parts by weight of a halogen-substituted organic compound
are added and meltmixed with the polyamide 4.6.

2. Process according to claim 1, characterized in that the copper salt is Cu(I) iodide.

3. Process according to claim 1 or 2, characterized in that the halogen-substituted organic compound is a brominated epoxy or styrene oligomer or polymer.

4. Process according to any of the claims 1-3, characterized in that 0.003-0.1 part by wt. of component (a) is present.

5. Process according to any of the claims 1-4, characterized in that 0.5-15 parts by weight of component (b) are present.

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EUROPEAN SEARCH REPORT

Application Number

EP 90 20 0715

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 281 691 (STAMICARBON)		C 08 L 77/06 // H 01 B 3/30 (C 08 L 77/06 C 08 K 3:16 C 08 K 5:00)
A	CHEMICAL ABSTRACTS, vol. 109, no. 22, 28th November 1988, page 54, abstract no. 191601y, Columbus, Ohio, US; & JP-A-88 142 059 (JAPAN SYNTHETIC RUBBER CO., LTD) 14-06-1988		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 08 K
C 08 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19-07-1990	LEROY ALAIN

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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